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A comparative dielectric study of poly(vinyl pyrrolidone) in unlike hydroxyl group number containing polar solvents

R J Sengwa[1*], Abhilasha[1], S C Mehrotra[2] and B R Sharma[3]

[1]Microwave Research Laboratory, Department of Physics, J N V University, Jodhpur-342 005, Rajasthan, India

[2]Department of Computer Science and Information Technology,
Dr. B A M University, Aurangabad-431 004, Maharashtra, India

[3]Department of Physics, Pratishthan Mahavidyalaya, Paithan, Aurangabad-431 007, Maharashtra, India

E-mail : rjsengwa@rediffmail.com

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Abstract : Time Domain Reflectometry (TDR) technique has been employed to explore the dielectric behaviour of different concentration binary mixtures of poly(vinyl pyrrolidone) (PVP) with ethyl alcohol, ethylene glycol, poly(ethylene glycol) (PEG) and glycerol in the frequency range of 10 MHz – 10 GHz at 25°C. The frequency-dependent measured values of dielectric permittivity ε' and dielectric loss ε'' of these binary mixtures were fitted to the Havriliak-Negami expression. It is found that PVP-ethyl alcohol mixtures exhibit Debye type dielectric dispersion whereas the complex dielectric behaviour of PVP-ethylene glycol, PVP-PEG and PVP-glycerol mixtures can be represented by Cole-Davidson dielectric relaxation model. The values of static dielectric constant ε_0, high frequency limiting dielectric constant ε_∞, relaxation time τ and distribution parameters α and β of these systems were determined. The types of the formation of homogeneous and heterogeneous cooperative domains in the mixtures due to complexation between hydroxyl group/s of polar solvent with the carbonyl groups of PVP molecular chain, were discussed using the comparative values of evaluated dielectric parameters. Schematic diagrams of the structures of a complexation between PVP and self-associated polar solvents were proposed and their dynamics have been explored in view of their applications in drug control release systems.

Keywords : Poly(vinyl pyrrolidone), polar solvents, dielectric behaviour, molecular dynamics, time domain reflectometry.

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1. Introduction

Recently [1–3], the structural-properties of non-toxic synthetic polymer *i.e.* poly(vinyl pyrrolidone) (PVP), dissolved with hydroxyl group/s containing solvent found their significant pharmaceutical usages. The solubility of PVP in hydroxyl group/s containing solvents, depends upon the formation of hydrogen bonds between the carbonyl group/s of the PVP monomer units and the hydroxyl groups of the solvent. Due to greater flexibility and mobility in PVP chain, its network in polar associating solvents can undergo to form various temporary structures at different concentrations of PVP in the solvent. Such structures are very useful in transdermal drug delivery system (TDDS). Adhesive, transport, reservoir, and biological properties of polymer composites constitute a general basis for their use as TDDS. PVP has TDDS properties and nature of the properties depends on the type of polar solvent used and the concentration of the PVP in the PVP-polar solvent mixtures.

In the present paper, an attempt has been made to explore the complex formation between carbonyl groups of PVP chain monomer units and the hydroxyl groups of polar solvents at different concentrations. Microwave dielectric relaxation spectroscopy has been employed to investigate the formation of homogeneous and heterogeneous intermolecular hydrogen bonding and their dynamics in complex system, because the microwave relaxation time of the reorientating molecules depends on their molecular size, shape, and intra- and intermolecular interactions. Further, the comparative dielectric study of macromolecules in different polar solvents is very interesting to confirm the structure changes of the

*Corresponding Author

macromolecules in different polar solvent environments. Keeping this objective in mind, the dielectric properties of PVP with ethyl alcohol (C_2H_5OH) (mono hydric alcohol), ethylene glycol ($HO\text{-}CH_2CH_2\text{-}OH$) and poly(ethylene glycol) [$H\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}OH$] (dihydric alcohol), and glycerol ($HO\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}OH$) (trihydric alcohol), bearing respectively, one, two and three hydrogen-bonding hydroxyl groups in their molecules, have been studied using time domain reflectometry (TDR) over the frequency range of 10 MHz to 10 GHz.

2. Experimental

Materials :

Poly(vinyl pyrrolidone) (PVP) of molecular weight 40000 g mol^{-1} and ethyl alcohol (E) of LR grade were obtained from Loba Chemie, India. The samples of ethylene glycol (EG) and poly (ethylene glycol) (PEG) (Mw = 400 g mol^{-1}) of LR grade were purchased from S.D. Fine-Chem, India. Glycerol (Gly) of AR grade was obtained from E. Merck, India. The binary mixtures of PVP-ethyl alcohol, PVP-ethylene glycol, PVP-PEG400 and PVP-glycerol were prepared at room temperature with PVP concentration (in wt%) variation. All mixtures were kept for almost 3 days to get PVP dissolved completely in the prepared binary mixtures. The maximum PVP concentration in different solvents is limited by the capacity of dissolution of PVP in the solvent and their increase in viscosity.

Dielectric measurements :

TDR technique was used to measure the permittivity ε' and dielectric loss ε'' of the PVP-ethyl alcohol (PVP-E), PVP-ethylene glycol (PVP-EG), PVP-PEG400, and PVP-glycerol (PVP-Gly) mixtures. All measurements were done in the frequency range 10 MHz – 10 GHz at 25°C. A HP 54750A-sampling oscilloscope with HP 54754A TDR plug-in module was used for measurements. Details of the apparatus and the procedures of the system have been reported elsewhere [4].

3. Data analysis

To evaluate various dielectric parameters, the frequency-dependent complex permittivity (ε^*) data of the binary mixtures were fitted by the least-square method to the Havriliak-Negami expression [5]

$$\varepsilon^*(\omega) = \varepsilon_\infty + [(\varepsilon_0 - \varepsilon_\infty)/(1 + j\omega\tau)^{1-\alpha}]^\beta, \qquad (1)$$

where $\varepsilon^* = \varepsilon' - j\varepsilon''$, ε' is known as dielectric permittivity and ε'' is known as dielectric loss. The values of static dielectric constant ε_0, dielectric constant at high frequency ε_∞, relaxation time τ and distribution parameters α and β of these molecules and their binary mixtures were obtained by fitting the experimental data into eq.(1).

Eq. (1) includes the Cole-Cole ($\beta = 1$) [6], Cole-Davidson ($\alpha = 0$) [7] and Debye ($\alpha = 0$; $\beta = 1$) [8] relaxation models. The free energy of activation ΔF_τ of these binary mixtures were calculated using Eyring's rate equation [9]

$$\Delta F\tau = RT \ln[(kT/h)\tau_0] \qquad (2)$$

The ratio (R) of the hydroxyl groups of ethyl alcohol, ethylene glycol, PEG400 and glycerol molecules, respectively, to the carbonyl groups of PVP monomer units were also determined in the prepared binary mixtures. The values of ε_0, ε_∞ relaxation strength $\Delta\varepsilon$, τ, α, β, ΔF_τ and R of these binary mixtures were recorded in Table 1. The evaluated values of ε_0 and τ of these mixtures with PVP concentration variation were also shown in Figure 1 for their comparison.

4. Results and discussion

Ethyl alcohol (E), ethylene glycol (EG), poly(ethylene glycol) (PEG) and glycerol (Gly) are self associated polar solvents. Due to the presence of hydroxyl group/s in their molecular structure, these molecules form the intermolecular associated linear polymeric or cross-linked clusters (local structures of self-associated molecules) with O–H····O linkage in dynamic equilibrium. The values of Kirkwood correlation factor g, which is the measure of the extent and strength of intermolecular hydrogen bonding for E, EG, PEG and Gly are 3.1, 2.4, 1.8 and 2.6, respectively [10,11]. The g values of these molecules greater than unity confirm that these intermolecular associations of alcohol molecules in pure liquid state tend to direct themselves with parallel dipole moment. Further, the comparative g values of these molecules confirms that the molecular association decreases as E > EG > PEG with increase in molecular size, although EG and PEG have two hydroxyl groups in their molecular structure. But the higher g value of Gly in comparison to EG and PEG is due to the presence of three hydroxyl groups in the molecular structure of Gly. Therefore, it is concluded that the molecular size and number of hydroxyl group/s in the molecular structure of these molecules affected their intermolecular structures. These polar liquids are good solvents for the non-toxic polymer poly(vinyl pyrrolidone) (PVP). When PVP is added into these inter-molecular self-associated polar solvents, it dissolved due to complex formation between the hydroxyl group/s of solvent molecules and the carbonyl groups of monomer units of randomly coiled PVP molecules. The complex

Table 1. Values of dielectric parameters of PVP-E, PVP-EG, PVP-PEG400 and PVP-Gly mixtures with varying concentration of PVP in mixtures at 25°C.

C_{PVP} wt%	ε_0	ε_∞	$\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$	α	β	τ (ps)	ΔF_τ (kcal mol^{-1})	R = -OH/-C=O
			PVP-Ethyl alcohol binary mixtures					
0	24.4	3.05	21.35			146.2	4.02	
5	23.8	3.58	20.22			148.9	4.03	48.2
10	23.4	3.62	19.78			159.2	4.07	24.1
15	22.9	3.62	19.28			155.9	4.05	16.1
20	21.6	3.64	17.96			151.7	4.04	12.1
40	19.9	3.60	16.30			150.5	4.03	8.0
50	19.0	3.67	15.33			155.3	4.05	4.8
60	17.9	3.66	14.24			169.3	4.10	4.0
80	16.9	3.63	13.27			175.4	4.12	3.0
100	15.6	3.60	12.00			163.3	4.08	2.4
140	14.4	3.57	10.83			176.7	4.13	1.7
			PVP-Ethylene glycol binary mixtures					
0	41.2	4.85	36.35	0.09	1.00	92.4	3.75	
10	38.2	4.70	33.50	0.79	0.96	130	3.94	35.79
20	32.8	4.68	28.12	0.80	0.95	145	4.01	17.90
30	29.4	4.82	24.58	0.805	0.92	166	4.09	11.93
40	23.8	4.59	19.21	0.78	0.91	175	4.12	8.95
			PVP-PEG400 binary mixtures					
0	17.3	4.68	12.62	0.09	0.79	129.2	3.94	
10	14.9	4.72	10.18	0.81	0.77	165.5	4.09	5.55
20	13.6	4.30	9.30	0.80	0.70	215	4.24	2.78
30	12.1	4.14	7.96	0.805	0.65	250	4.33	1.85
			PVP-Glycerol binary mixtures					
0	42.5	4.92	37.58	0.041	0.944	1223.71	5.26	
5	40.44	4.18	36.26	0.085	0.897	744.72	4.97	72.39
10	39.86	4.31	35.55	0.088	0.893	745.30	4.97	36.19
15	38.60	4.34	34.26	0.092	0.889	751.28	4.98	24.14
20	36.79	4.35	32.44	0.094	0.886	749.52	4.98	18.09
25	34.99	4.33	30.66	0.098	0.882	751.44	4.98	14.47

formation produces the orientation of the solvent molecules around PVP chain, due to which there may be change in the self-associated structure of the solvent molecules and also in their dynamics. To confirm the molecular dynamics of these solvents in PVP matrix, different PVP concentration C_{PVP} binary mixtures were prepared (Table 1). In these mixtures, the ratio of solvent hydroxyl groups (-OH) to the PVP carbonyl groups (C = O) *i.e.* R=OH/C=O (Table 1) is greater than one. If it is assumed that all the carbonyl groups of the PVP activated with the hydroxyl groups of the solvent in these prepared mixtures, there are presence of uncomplexed hydroxyl groups. Earlier, Feldstein *et al* [3,12–14] studied the stoichiometry of PVP with hydroxyl group/s containing solvents and confirmed that all carbonyl groups of PVP repeat units cannot form hydrogen bonds with the hydroxyl groups of the solvent in the mixtures. Due to this, there is existence of homogeneous structure of the solvent in the PVP-hydroxyl group/s containing solvent mixtures. Therefore in the prepared mixtures, two types of cooperative domains (CDs) can be assumed. CD_{sol} that includes the self-associated solvent molecules and $CD_{PVP\text{-}sol}$, which includes the solvent molecules those interacted directly with PVP chain. The dynamics of solvent clusters (CD_{sol}) is very important in the release of drug loaded in such type of mixtures matrix. The drug loading ability in the matrix

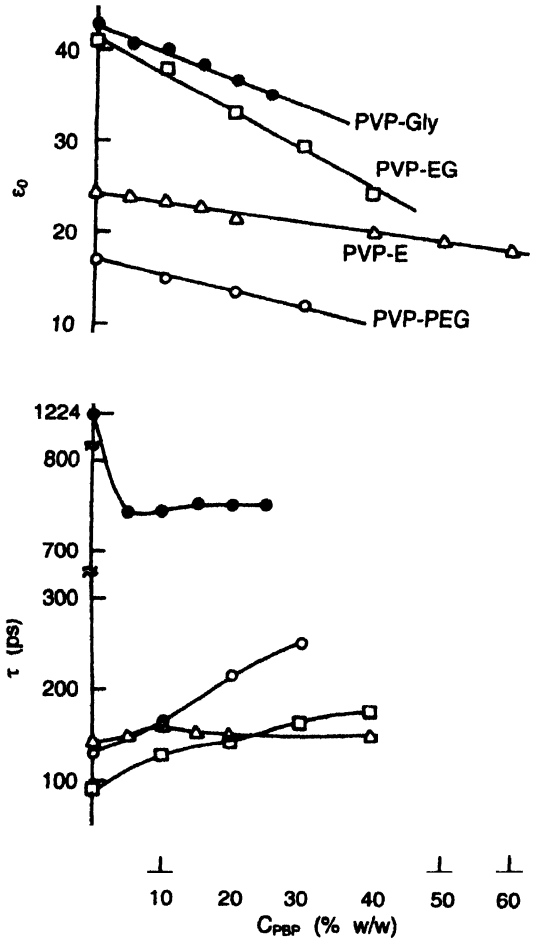

Figure 1. Static dielectric constant (ε_0) and relaxation time (τ) of PVP-E, PVP-EG, PVP-PEG and PVP-Gly mixtures as a function of concentration of PVP (%w/w).

depends on the free volume created in the matrix, which depends on the solvent molecular size. The comparative microwave dielectric relaxation studies of these mixtures is used to explore the nature of the formation of homogeneous and heterogeneous cooperative domains and the dynamical structures of PVP-hydroxyl group/s containing solvents in view of their usages in drug control release systems.

(i) Molecular dynamics in PVP-E mixtures :

The dielectric dispersion behaviour of E and PVP-E mixtures is a simple Debye type ($\alpha = 0$; $\beta = 1$). The evaluated ε_0, τ and ΔF_τ values of E and PVP-E mixtures are shown in Table 1. Molecules with intermolecular hydrogen bonds have high values of ε_0 and τ [10,11,15–17]. Earlier [11,18], using dielectric parameters, it is confirmed that the molecules of ethyl alcohol form H-bonded linear polymeric clusters. The higher τ value of E molecules confirmed that there is large steric hindrance to the reorientational motion of polymeric homogeneous chains of ethyl alcohol molecules. In ethyl alcohol, the molecular motion is interpreted by considering the rotational tumbling of long-lived clusters (switch-over type mechanism) and the internal fluctuations *i.e.* association-dissociation dynamics [18–21].

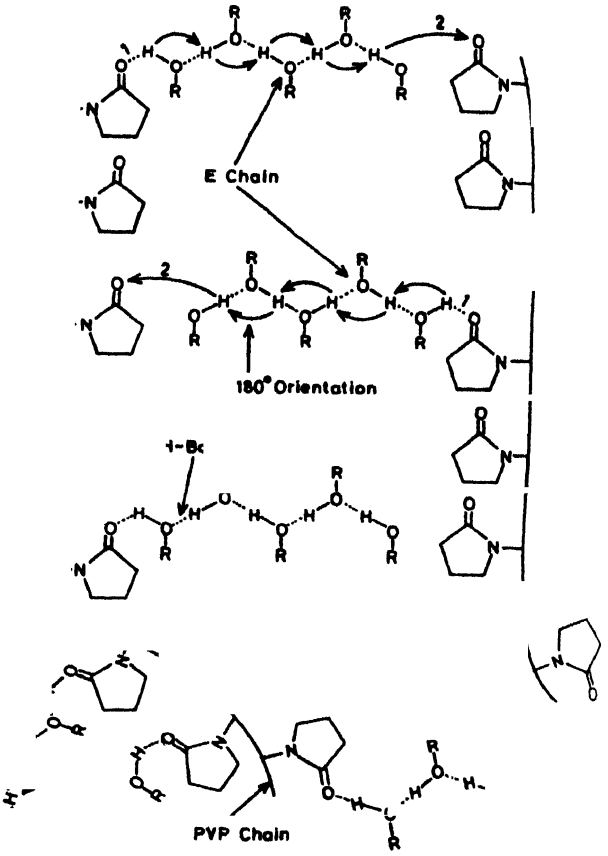

Figure 2. Schematic diagram of the proposed structure of a complex between high-molecular-mass PVP and homogeneous short-chain of E, with the 180° orientation of hydroxyl groups in the E chain and the transition of PVP-E complex from position 1 to position 2.

In binary mixtures of PVP-E, the complexed structure of CD_E and $CD_{PVP\text{-}E}$ can be assumed as sketched in Figure 2. The structure of ethyl alcohol molecules in PVP matrix is considered as suggested by the earlier workers [18–21]. The observed values of ε_0, τ and ΔF_τ of PVP-E mixtures support the assumed structures shown in Figure 2. The linear decrease of ε_0 with the increase in PVP concentration in PVP-E mixtures (Table 1, Figure 1) is due to the volume effect arising from the addition of large molecular size PVP. The Debye type dielectric dispersion of PVP-E mixtures confirms the reorientational motion of self-associated E molecules in the PVP matrix, which is due to either rotational tumbling or formation and deformation of $CD_{PVP\text{-}E}$. Comparatively small anomalous increase in τ values with the increase in PVP concentration, confirms that the hindrance to the reorientational motion of E molecules also varies. This variation in hindrance of rotating E molecules may be

due to the change in the size of the reorientating CD_E with the decrease in the ratio of hydroxyl groups to the carbonyl groups in the PVP-E mixtures (Table 1). The values of ΔF_τ of E and PVP-E mixtures are in agreement with the activation energy required for the breakage of hydrogen bond. This suggests that the dynamic state of formation and deformation of H-bonds between carbonyl groups and hydroxyl groups as sketched in Figure 2. The switch-over type mechanism of E molecules break the O–H····O bond at the ends of their linear polymeric chain structure and then rotate through 180° and switching occurs cooperatively all along the multimer chain (Figure 2) of E molecules complexed with the monomers of PVP chain. From the observed τ values of PVP-E mixtures, it seems that the overall molecular dynamics of CD_E is less influenced by the formation of $CD_{PVP\text{-}E}$. Earlier [18], dielectric relaxation studies of PVP-E mixtures in non-polar solvents *i.e.* benzene, also confirmed that the dynamics of CD_E in PVP-E mixtures in quasi-isolated state, significantly influences by the concentration of the PVP, which is due to the large variation in the elongation of the transient structure of PVP-E in dilute solutions.

(ii) Molecular dynamics in PVP-EG and PVP-PEG mixtures :

The dielectric dispersion behaviour of EG is Cole-Cole type. Table 1 shows that its ε_0 value is much higher than the ε_0 value of ethyl alcohol which is due to the presence of two hydroxyl groups in the molecular structure of EG. The ε_0 value of PEG is lower than the ε_0 values of EG and E. Although PEG molecules have hydroxyl groups at two ends, the increase in number of carbon atoms in its molecular structure, reduces the value of ε_0. The dielectric dispersion of PEG and PVP-PEG mixture is Cole-Davidson type. The observed distribution parameters α and β of these systems are recorded in Table 1.

The g values of EG and PEG confirmed that due to intermolecular association there is larger probability of linear polymeric H-bonded structure of these molecules. The addition of PVP in EG makes the asymmetric dielectric dispersion behaviour of PVP-EG mixtures (Cole-Davidson type). The ε_0 values of PVP-EG and PVP-PEG mixtures decrease almost linearly with the increase in the PVP concentration but their τ values increases. The observed τ values of these mixtures suggest that there is reorientation of the homogeneous cooperative structure of the solvent molecules in the PVP matrix. The increase in τ values with the increase in PVP concentration also shows that the hindrance to the molecular reorientation of CD_{sol} increases, which may be due to the increase in the complexation of hydroxyl groups with the carbonyl groups of PVP molecules. The structure of PVP-EG molecules with the CD_{EG} and $CD_{PVP\text{-}EG}$ is sketched in Figure 3. The linear behaviour of CD_{EG} is assumed with the formation and deformation of hydrogen bonds in dynamic equilibrium.

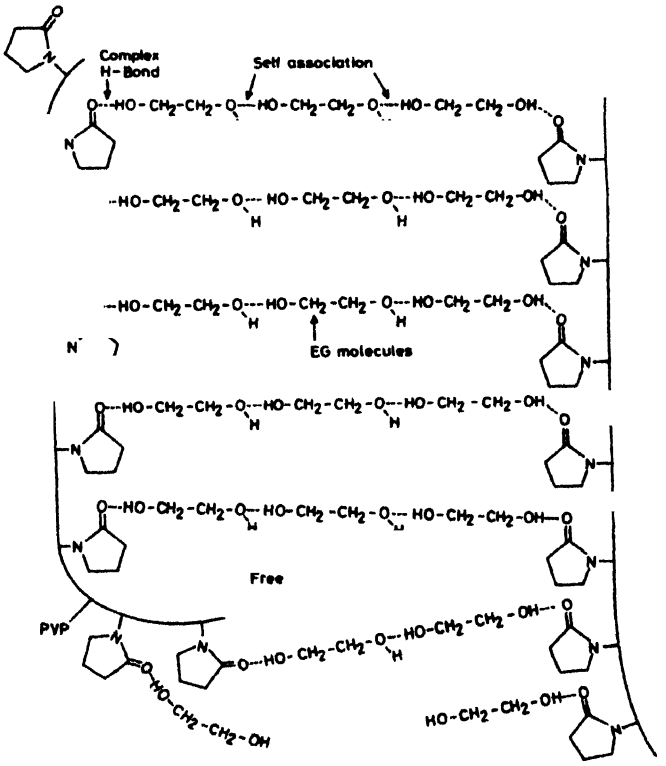

Figure 3. Schematic diagram of the proposed structure of a complex between PVP and linear self-associated EG.

Earlier [10], it is confirmed that the chain of PEG400 molecules is flexible and there is larger probability of the intermolecular self-association in coiled form. When the high flexible chain PVP molecules are added into liquid PEG400, then due to complexation between ends, hydroxyl groups of PEG and carbonyl groups of PVP chain dissociate the self-association of PEG molecules. Such complex formation between PVP and PEG400 molecules stretch the chain of PEG molecules as shown in Figure 4. The stretched PEG molecules align parallel to each other and form the supramolecular structures in PVP matrix (Figure 4.) Feldstein *et al* [12] also proposed the supramolecular structure of PVP-PEG molecules in dynamic equilibrium using FTIR spectroscopy of PVP-PEG mixtures. Further, the increase in τ values of PVP-PEG mixtures also confirms that the complex formation between PEG ends hydroxyl groups and carbonyl groups of PVP are stronger in comparison to the self-association of PEG molecules. In PEG molecules, there is

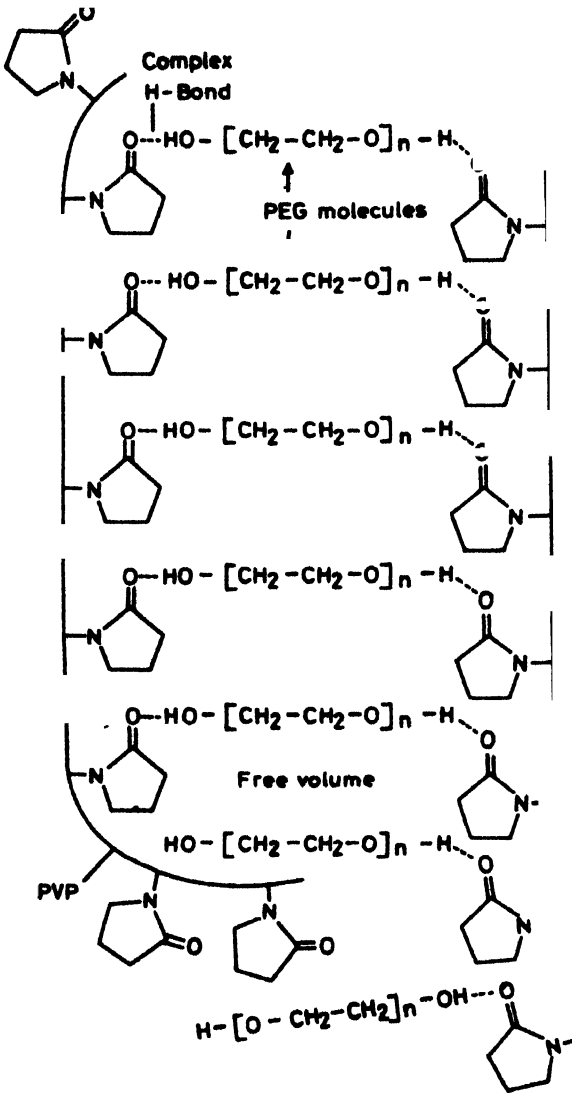

Figure 4. Schematic diagram of the proposed structure of a complex between PVP and short-chain PEG.

reorientation of ends hydroxyl groups in dynamic equilibrium with the formation of five membered intramolecular ring [10]. This behaviour of ends hydroxyl groups helps the reorientation of PEG molecules. Further, the observed ΔF_τ values of these mixtures (Table 1) also support the dynamical behaviour of PEG molecules in PVP matrix due to formation and deformation of complexes. Stockhausen and Abd-El-Rehim [22] also explored the viscosity-independent relaxation behaviour of PVP-PEG mixtures. The dielectric relaxation behaviour of PVP-PEG mixtures in dilute solutions of non-polar solvents *i.e.* benzene and dioxane, confirmed that the non-polar solvent environment significantly influences the dynamics of PEG molecules in PVP-PEG mixtures [23,24] but their dynamics in dilute solutions is independent of the mixture viscosity.

(iii) Molecular dynamics in PVP-Gly mixtures :

Glycerol (Gly) molecule is made of two primary alcohol groups and one secondary alcohol group. The primary alcohol groups of Gly are more reactive than the secondary alcohol group. The higher g value of Gly in comparison to the g values of EG and PEG molecules suggest that there is crosslinkage H-bonded structure of Gly molecules due to the presence of secondary alcohol hydroxyl group in its molecular structure. The Cole-Davidson dielectric dispersion behaviour of Gly also suggests the crosslinked *i.e.* branched chain molecular structure of Gly molecules. The large τ value of Gly molecules is due to the longlive crosslinked structure formed by the secondary hydroxyl groups of Gly molecules.

The slow dissolution of PVP in Gly at room temperature shows that dissociation of homogeneous Gly structure CD_{Gly} takes longer time to form the complexes between PVP carbonyl groups with Gly hydroxyl groups. The dielectric dispersion of PVP-Gly molecules is also found to be of Cole-Davidson type. But there is large decrease in τ values of these mixtures, which suggest that the dynamics of CD_{Gly} increases by the complex formation with PVP in PVP matrix in comparison to their dynamics in pure liquid state. Further, Table 1 shows that the τ values of PVP-Gly mixtures are independent of the PVP concentration. Although the viscosity of these mixtures increases significantly with PVP concentration, the observed τ values of the mixture confirm that the dynamics of Gly clusters in PVP matrix is independent of the mixture viscosity. The stoichiometry [25] of PVP-Gly complexes also suggest that in case of Gly overload compositions, more than 80% of PVP units are found crosslinked whereas in PVP-PEG network, nearly 30 mol% of PVP repeat units form complexes within a wide mixture range. The remaining 70 mol% of PVP units are either intact or loosely bound through one hydroxyl group of PEG only. The breaking of large order CD_{Gly} and formation of $CD_{PVP\text{-}Gly}$ in PVP-Gly mixtures is also supported by the comparative τ values of these systems. The crosslinked dynamical structure of the Gly molecules in PVP matrix can be assumed as sketched in Figure 5. The ΔF_τ values of Gly and PVP Gly were found to be nearly 5 kcal mol^{-1}, which is nearly 1 kcal mol^{-1} higher in comparison to the ΔF_τ values of PVP-E, PVP-EG and PVP-PEG systems. The higher ΔF_τ values of Gly and PVP-Gly also show the larger hindrance to the molecular reorientation of Gly clusters due to hydrogen bonding. The ε_0 values of PVP-Gly decrease with the increase in PVP concentration. The variation of ε_0 and τ of all the studied binary mixtures are shown in Figure 1.

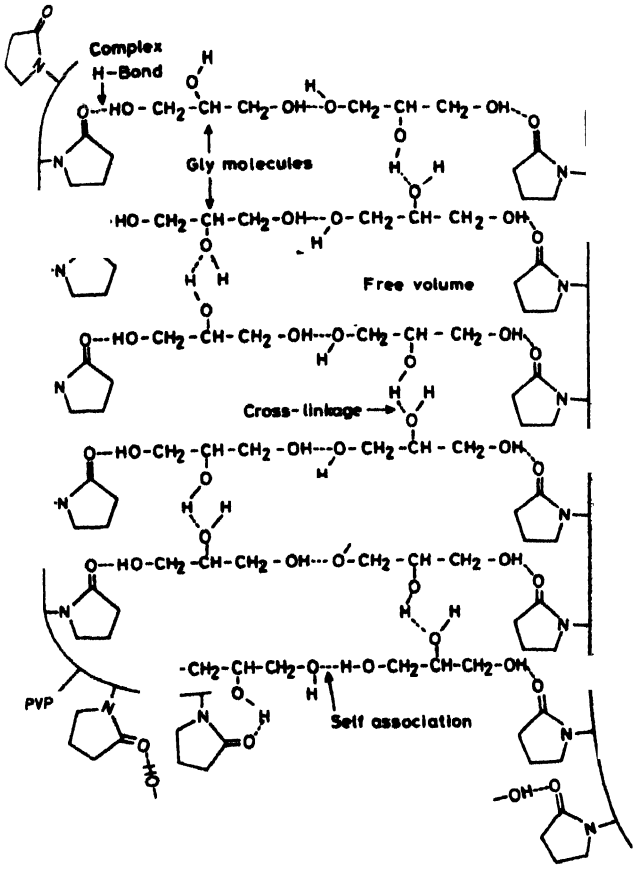

Figure 5. Schematic diagram of the proposed structure of a complex between PVP and cross-linked self-associated Gly.

From Figure 1, it is observed that the static dielectric constant $\varepsilon_{0\ (PVP\text{-}sol)}$ of the studied PVP-solvent mixtures depends on the PVP concentration by the linear relation as

$$\varepsilon_{0\ (PVP\text{-}sol)} = \varepsilon_{sol} + \delta C_{PVP}, \quad (3)$$

where C_{PVP} is the concentration of PVP in solvent, ε_{sol} represents the static dielectric constant of pure solvent and δ is the constant (known as the dielectric decrement). The dielectric decrement δ determined from Figure 1 decreases in the order EG ($\delta_{PVP\text{-}EG}$ = –0.42) > Gly ($\delta_{PVP\text{-}Gly}$ = –0.30) > PEG ($\delta_{PVP\text{-}PEG}$ = –0.20) > E ($\delta_{PVP\text{-}E}$ = –0.11). This sequence clearly disagrees with the order of the solvent molecular sizes. From δ values, it can be concluded that the structuring effects of the solvents on PVP are more important for the static dielectric constant of the PVP-solvent mixtures examined than the large size PVP macromolecules volume effects. The PVP molecules as shown in Figures 2–5, bind and orient the solvents molecules around them, reducing their ability to orient in the applied field, and so reducing the dielectric constant. The observed δ values shows that the PVP molecules bind and orient the EG molecules maximum in comparison to the other used solvents. From the δ values, it seems that the order of the orientation of the solvent molecules by PVP in decreasing order is as EG > Gly > PEG > E. It is according to the molecular behaviour of these pure solvents. In case of E molecules due to their switch-over mechanism behaviour, the reorientation of E molecules by PVP is minimum among these solvents. The complexed PEG molecules with PVP chain, align themselves parallel by their orientation and form super-molecular structure as shown in Figure 4. The orientation of EG molecules after complexation with PVP is maximum and hence the linear self-associated EG molecules bridges the PVP chain as sketched in Figure 3. Due to cross-link association in Gly molecules, there is less orientation of Gly molecules with PVP complexation in comparison to the orientation of EG molecules to form complexation with linear structure of EG molecules in presence of PVP.

5. Conclusions

The complex formation between hydroxyl groups and carbonyl groups of PVP in the binary mixtures of PVP-E, PVP-EG, PVP-PEG and PVP-Gly were explored using the comparative microwave dielectric behaviour of these systems. The dynamics of hydroxyl group/s containing solvents in PVP matrix strongly depends on the presence of number of hydroxyl group/s in the solvent molecules and the size of the solvent molecules. The reorientation motion of the solvent structure in PVP matrix is due to the continuous formation and deformation of hydrogen bonds in dynamic equilibrium. In these systems, the molecular dynamics is found to be independent of the solution viscosity. In PVP-monohydric alcohol, the PVP matrix is less affected by the molecular dynamics of the solvent but PVP matrix produces large hindrance to the dynamics of dihydric alcohols and the hindrance to molecular reorientation increases with the increase in PVP concentration. In case of trihydric alcohol, the presence of PVP matrix helps the molecular dynamics of homogeneous clusters of Gly molecules, but the molecular dynamics is independent of the increase in PVP concentration. The structures of PVP-solvents were sketched on the basis of the comparative values of their dielectric parameters. These sketched structures of different alcohols in PVP matrix can be used to understand the rate of release of the drug when loaded in these H-bonded complexed PVP matrix, because these systems have enhanced free volume and large molecular mobility with adhesion properties.

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